Poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) amphiphilic polymer conetworks and gels

Ph.D. Theses

Csaba Fodor

Eötvös Loránd Science University, Faculty of Natural Sciences
Doctorate School of Chemistry
Synthetic Chemistry, Material Science, Biomolecular Chemistry Program

Doctorate School Leader: Prof. György Inzelt
Program Leader: Prof. András Perczel
Supervisor: Prof. Béla Iván

Budapest
2011

Poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) amphiphilic polymer conetworks and gels

Ph.D. Theses

Csaba Fodor

Budapest
2011

I. Introduction and Objectives

Polymer chemistry and related material science are progressive areas for the synthesis and investigations of novel amphiphilic conetworks (APCNs) with unique nanophasic structures. Polymer conetworks are multiphase assemblies consisting of at least two different immiscible hydrophilic and hydrophobic polymer chains connected with chemical bonds to each other. This prevents macroscopic phase separation, and thus unique phased separated structures are obtained. The phase separated structure provides special properties for such conetworks, which may open several ways to the material science investigations and biomedical utilization as well.

In the course of my Ph.D. studies, my goal was to synthesize new amphiphilic polymer conetworks on the basis of the hydrophilic poly(*N*-vinylimidazole) (PVIm) combined with hydrophobic poly(tetrahydrofuran) (PTHF) cross-linkers having different molecular weights. A broad composition range of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) amphiphilic conetwork samples was planned („*l*" stands for „*linked by*"). The properties of the PVIm-*l*-PTHF conetworks were investigated by different analytical techniques, like elemental and thermal analyses, thermal stability tests, as well as swelling experiments and structural characterizations. Swelling experiments were carried out in both polar (water, methanol) and non-polar (tetrahydrofuran, carbon tetrachloride) solvents. The nanostructure of the conetworks and the complexation ability of the hydrophilic phase were utilized in preparing organic-inorganic nanohybrid materials. To utilize the APCNs as nanoreactors, the metal ion binding ability of the hydrophilic phase was investigated by qualitative as well as quantitative measurements and analytical methods. The size distribution and morphology of the polymer matrix with the embedded nanostructures and the antimicrobial effect were also studied.

The primary aims of my Ph.D. studies were the synthesis of PVIm-*l*-PTHF conetworks followed by thorough investigations of the properties and structure together with the preparation and exploration of the nanohybrid materials based on amphiphilic conetworks.

II. Applied Methods

A series of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) amphiphilic conetworks was prepared via free radical copolymerization of poly(tetrahydrofuran) macromonomer and *N*-vinylimidazole monomer. The poly(tetrahydrofuran) macromonomers were synthesized via cationic ring-opening polymerization and the analyses were performed by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy. The syntheses of the conetworks were performed in a special teflon mold under nitrogen atmosphere. The conetworks were purified by extraction with tetrahydrofuran and methanol. The structure of the amphiphilic conetworks was investigated by several analytical methods. The composition was determined by elemental analysis, the phase separated morphology was proved by phase mode atomic force microscopy (AFM), the thermal properties and thermal stability were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The swelling behavior of the conetworks was measured gravimetrically in both polar and non-polar solvents. The metal ion sorption ability of the hydrophilic poly(*N*-vinylimidazole) was measured by ^{13}C NMR and flame atomic absorption spectroscopy (FAAS). Transmission electron microscopy (TEM) was used for the study of the size distribution and morphology of the nanoparticles.

III. Major Scientific Results

1.

Successful synthesis of a PVIm-*l*-PTHF amphiphilic conetwork series with different molecular weight poly(tetrahydrofuran) dimethacrylate macromonomers (M_n = 2170 g/mol, M_w/M_n = 1.65 és M_n = 9860 g/mol, M_w/M_n = 1.21) in a wide range of composition was carried out. In the conetwork series with lower molecular weight poly(tetrahydrofuran), the cross-linker content varied between 25 and 89 wt%, and in the case of the higher one conetworks with 46 to 91 wt% PTHF were obtained. The swelling behavior of the conetworks was measured in both polar and nonpolar solvents. The results indicate that the swelling degrees depend on the composition in each solvent. The swelling ratio increases in nonpolar solvents with the hydrophobic PTHF content. In polar solvents, an opposite tendency is predominate.

2.

The swelling kinetics was investigated in water and in tetrahydrofuran. The swelling degrees as a function of time indicate that the swelling process of the PVIm-*l*-PTHF conetworks in water and THF proceeds with a non-Fickian, but with composition dependent anomalous diffusion.

3.

The phase behavior of the conetworks was investigated with differential scanning calorimetry (DSC). The PVIm-*l*-PTHF samples possess two distinct glass transition temperature (T_g) values in good accordance with the homopolymer components. The two T_gs indicate that the PVIm and PTHF phases of the conetworks do not mix with each other, but they form phase separated structure. Morphology studies of the conetworks were performed by atomic force microscopy (AFM), which indicates separated phases with 5-30 nm domain sizes. The morphology depends on the composition. At the composition margins, the domains are spherical and dispersed in the major continuous matrix. In the middle of the composition range, both phases are continuous in each other, that is the PVIm-*l*-PTHF conetworks possess special cocontinuous nanophasic morphology.

4.

The thermal analysis (DSC) of the PVIm-*l*-PTHF conetworks indicates that the crystalline fraction (X_c) of the conetworks change with the relative PTHF content. In the conetworks with the lower molecular weight PTHF cross-linker, X_c varies between 4.5 and 15.2%, and with the higher molecular weight PTHF the crystalline fraction of the PTHF component is between 31.3 to 44%. These X_c values are far below of that of the pure homopolymers in all cases. The melting temperature (T_m) of the microcrystals in the macroscopically homogenous conetworks is lower than that of the T_m of the pure homopolymers. The fraction of crystalline phase of PTHF and the melting point of these crystals are influenced by the composition, the lower the PTHF content, the lower the melting point.

5.

The metal ion binding ability of the conetworks was studied by different analytical methods. For the qualitative metal ion binding study, solid state ^{13}C NMR was used. The results indicate that only the hydrophilic PVIm phase interact with the metal ions. The hydrophobic PTHF phase may act as reactor wall around the hydrophilic phases, therefore these

conetworks can be considered as nanoreactors. The metal ion binding capacity of the conetwork samples were quantitatively measured by flame atomic absorption spectroscopy (FAAS). The quantitative results indicate composition dependent metal ion sorption. The recyclable complexation of the conetworks was also investigated. The experimental results clearly show that the PVIm-*l*-PTHF conetworks can be used for several binding-eluting cycles without any significant capacity loss.

6.

The nanoreactor principle was confirmed by the complexation ability of the hydrophilic PVIm phase. After swelling this phase with copper ion containing aqueous solution in order to bring these metal ions into the conetworks, reduction of the copper ions with hydrazine was carried out in inert atmosphere. This process led to the formation of copper nanoparticles inside and on the surface of the conetworks. The formation of these nanoscale particles in the resulting nanohybrids was confirmed by electron diffraction analysis performed by the TEM. Depending on the reduction time with aqueous hydrazine solution, copper oxide (cuprite, Cu_2O) or copper nanoparticles were formed.

7.

PVIm-*l*-PTHF/nanosilver hybrids were also synthesized by reduction of the silver ions in the hydrophilic PVIm phase of the conetworks. Several bacterial strains were used to confirm the antimicrobial effect of these new nanohybrids materials.

IV. Conclusions

In the course of my Ph.D. studies, the synthesis, the structure and the properties of poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) (PVIm-*l*-PTHF) amphiphilic conetworks were widely investigated. Totally new materials with unique structures were synthesized. These new conetworks possess nanophase separated cocontinuous morphology, which are potential nanotemplates for copper and silver nanohybrids. It was experimentally proved that the nanosilver containing PVIm-*l*-PTHF conetworks possess antimicrobial effect. These new results allow to expand the utilization of the PVIm-*l*-PTHF conetworks not only for the

medical field, but also to environmental protection and nanotechnologies through the heavy metal ion sorption ability of the conetworks.

V. Publication list

1. B. Iván, Cs. Fodor, G. Kali, P. Mezey, R. Thomann, R. Mülhaupt: „Nanophasic Amphiphilic Conetworks and New Nanohybrids Thereform" *Polym. Mater. Sci. Eng.*, **2009,** *100,* 267-268.
2. B. Iván, A. Domján, G. Erdődi, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, Á. Szabó, S.L. Szabó, I. Szalai, R. Thomann, R. Mülhaupt: „Smart Nanostructured Amphiphilic Polymer Conetworks" *Polym. Mater Sci. Eng.*, **2009,** *101,* 925-926.
3. Cs. Fodor, G. Kali, B. Iván: „Poly(*N*-vinylimidazole)-*l*-Poly(tetrahydrofuran) „Amphiphilic Conetworks and Gels: Synthesis, Characterization, Thermal and Swelling Behavior" *Macromolecules* **2011**, *44*, 4496-4502.
4. Cs. Fodor, B. Iván: „Poly(*N*-vinylimidazole)-*l*-Poly(tetrahydrofuran) Amphiphilic Conetworks and Gels. II. Unexpected Dependence of the Reactivity of Poly(tetrahydrofuran) Macromonomer Cross-Linker on Molecular Weight in Copolymerization with *N*-Vinylimidazole" *J. Polym. Sci., Part A: Polym. Chem.* **2011,** *49,* ASAP, DOI: 10.1002/pola.24972
5. Cs. Fodor, R. Thomann, Y. Thomann, G. Kali, B. Iván, R. Mülhaupt: „"Chameleon" Amphiphilic Conetworks with Broad Composition Window of Bicontinuous Nanpphasic Morphologies"
   (in manuscript)
6. Cs. Fodor, B. Iván: „Poly(*N*-vinylimidazole)-*l*-Poly(propylene oxide) Amphiphilic Conetworks"
   (in manuscript)
7. A. Domján, Cs. Fodor, Sz. Kovács, T. Marek, B. Iván, K. Süvegh, A. Vértes: „Anomalous Swelling Behavior of Poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran) Amphiphilic Conetwork in Water Studied by Solid-state NMR and Positron Annihilation Lifetime Spectroscopy"
   (in manuscript)

VI. Conference Presentation list

1) Fodor Cs.:
   Poli(*N*-vinil-imidazol)-*l*-poli(propilén-oxid) kotérhálók
   Undergraduate Student Conference, Eotvos Lorand University Faculty of Science Institute of Chemistry, Budapest, Hungary, December 3, 2005
2) Fodor Cs.:
   Poli(*N*-vinil-imidazol)-*l*-poli(propilén-oxid) kotérhálók
   Nationwide Undergraduate Student Conference, Szeged, Hungary, April 1-4, 2006
3) B. Iván, Cs. Fodor, P. W. Groh, M. Haraszti, P. Mezey, V. Pálfi, S. L. Szabó:
   Polymers and gels in DNA delivery and medical practice
   Asboth Oszkar Innovation Program 2005, Kick off Meeting, Mátraháza, Hungary, March 16-18, 2006
4) Cs. Fodor, B. Iván:
   Poly(*N*-vinylimidazole)-*l*-poly(propylene oxide) Amphiphilic Conetworks
   1st European Chemistry Congress, Budapest, Hungary, August 27-31, 2006 (poster)
5) Fodor Csaba, Kali Gergely, Zihné Perényi Katalin, Iván Béla:
   N-vinil-imidazol alapú amfifil kotérhálók szintézise, analízise és réz(II)-ion megkötő képességének vizsgálata
   HAS Chemical Research Center, Scientific Days, Budapest, Hungary, May 22-24, 2007
6) Domján A., Hódi K., Varga J., Mezei P., Fodor Cs., Kali G., Iván B.:
   Makromolekulák és összetett polimerrendszerek vizsgálata szilárd fázisú NMR-módszerekkel
   HAS Chemical Research Center, Scientific Days, Budapest, Hungary, May 22-24, 2007
7) Cs. Fodor, G. Kali, B. Iván:
   Synthesis, characterization and metal ion binding of *N*-vinylimidazole based amphiphilic conetworks
   European Polymer Congress, Portoroz, Slovenia, July 2-6, 2007 (poster)
8) Cs. Fodor, G. Kali, K. Z. Perényi, B. Iván:
   Synthesis, Characterization and Copper(II) Ion Coordination Studies of Amphiphilic Conetworks Based on *N*-Vinylimidazole
   11th Dresden Polymer Discussion, Dresden (Meissen), Germany, September 16-19, 2007 (poster)

9) Cs. Fodor, G. Kali, K. Z. Perényi, A. Domján, B. Iván:
Metal ion binding by water swollen poly(*N*-vinylimidazole)-*l*-poly(tetrahydrofuran), a novel amphiphilic conetwork
9th Confeence on Colloid Chemistry, Siófok, Hungary, October 3-7, 2007 (poster)

10) Erdődi G., Fodor Cs., Groh Werner P., Haraszti M., Iván B., Kali G., Mezey P., Pálfi V., Soltész A., Szabó L.S., Szanka I., Szarka Gy., Verebélyi K.:
Új nanoszerkezetű polimer rendszerek, mint új nanohibrid anyagok platformja
Feast of the Hungarian Science 2007, Budapest, Hungary, November 14, 2007 (poster)

11) Erdődi G., Fodor Cs., Groh Werner P., Haraszti M., Hellner Á., Iván B., Kali G., Kasza Gy., Mezey P., Pálfi V., Soltész A., Szabó L.S., Szanka I., Szarka Gy., Verebélyi K.:
Nanoszerkezetű polimereken alapuló új nanohibrid anyagok
ELTE Innovation Day, Budapest, Hungary, February 5, 2008(poster)

12) Fodor Csaba, Kali Gergely, Domján Attila, Zihné Perényi Katalin, Iván Béla:
N-vinil-imidazol alapú amfifil kotérhálók szintézise és alkalmazhatósága nehézfémionok megkötésében
VIII. Winter school, Balatonfüred,. February 06-08, 2008

13) E. Velickova, P. Petrov, Cs. Fodor, V. Manojlovic, V. Nedovic, B. Ivan, E. Winkelhausen, Ch. Tsvetanov:
New carriers for cell immobilization
6th International Conference of the Chemical Societies of the South-Eastern European Countries, Sofia, Bulgaria, September 10-14, 2008

14) B. Iván, G. Erdődi, A. Domján, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, J. Scherble, R. Thomann, R. Mülhaupt:
Amphiphilic conetworks: new nanostructured polymers for smart materials, nanohybrids and biomaterials
9th Austrian Polymer Meeting, Graz, Austria, March 26-28, 2008,

15) B. Iván, G. Erdődi, A. Domján, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, J. Scherble, R. Thomann, R. Mülhaupt:
Nanophasic amphiphilic polymer conetworks: a new material platform for nanostructured surfaces and films
1st Functional Nanocoatings Conference, Budapest, Hungary, March 30 - April 2, 2008

16) Cs. Fodor, G. Kali, K. Z. Perényi, A. Domján, B. Iván, R. Thomann, R. Mülhaupt:
Heavy metal ion chelating by water swollen *N*-vinylimidazole based nanophasic amphiphilic conetwork films

1st Functional Nanocoatings Conference, Budapest, Hungary, March 30 - April 2, 2008 (poster)

17) Cs. Fodor, G. Kali, K. Z. Perényi, A. Domján, R. Mülhaupt, R. Thomann, B. Iván: Preparation, characterization of polymer conetworks as metal ion chelating agents Polymer Network Group Conference, Larnaca, Cyprus, June 22-26, 2008 (poster)

18) B. Iván, Cs. Fodor, G. Kali, P. Mezey R. Thomann, R. Mülhaupt: Nanophasic amphiphilic conetworks and new nanohybrids therefrom American Chemical Society Meeting, Salt Lake City, US, March 22-26, 2009

19) B. Iván, Cs. Fodor, P. Mezey, G. Kali, A. Domján, R. Thomann, R. Mülhaupt: Novel nanophasic amphiphilic polymer conetworks as new material platform for speciality nanohybrids
International Conference on Nanostructured Polymers and Nanocomposites, Paris, France, April 15-17, 2009

20) Cs. Fodor, B. Iván, G. Kali, P. Mezey, S. Szabó, R. Thomann, R. Mülhaupt: Nanophasic amphiphilic polymer conetworks as a new material platform for organic-inorganic nanohybrids
Frontiers in Polymer Science, Mainz, Germany, June 7-9, 2009(poster)

21) B. Iván, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, S. Szabó, R. Thomann, R. Mülhaupt:
Bicontinuous nanophasic amphiphilic polymer conetworks as a new material platform for specialty nanohybrids
European Polymer Congress, Graz, Austria, July 12-17, 2009

22) Fodor Csaba, Domján Attila, Kali Gergely, Zihné Perényi Katalin, Német Péter, Iván Béla, Ralf Thomann, Rolf Mülhaupt:
Poli(*N*-vinil-imidazol) alapú polimer kotérhálók és nanohibridek
Hungarian Academy of Sciences Plastics and Natural Polymers Work Committee, Budapest, Hungary, April 23, 2009

23) B. Iván, A. Domján, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, S. Szabó, R. Thomann, R. Mülhaupt:
Nanophasic amphiphilic polymer conetworks as a new material platform for specialty nanohybrids
8th International Conference on Advanced Polymers Via Macromolecular Engineering (APME 2009), Dresden, Germany, October 4-7, 2009

24) B. Iván, A. Domján, G. Erdődi, Cs. Fodor, M. Haraszti, G. Kali, P. Mezey, Á. Szabó S. L. Szabó, I. Szalai, R. Thomann, R. Mülhaupt:
Smart nanostructured amphiphilic polymer conetworks
238th ACS National Meeting, Washington, DC, US, August 16-20, 2009

25) Iván B., Fodor Cs., Mezey P., Domján A., Haraszti M., Kali G., Szabó S., Thomann R., Mülhaupt R.:
Nanoszerkezetű amfifil kotérhálók, mint nanohibrid anyagok új platformja
National Material Science Conference, Balatonkenese, Hungary, October 11-13, 2009

26) Fodor Cs., Iván B.:
Fémion megkötésére alkalmas amfifil polimer kotérháló
Hungarian Academy of Sciences, Colloid Chemistry and Material Science Work Committee, Mátrafüred, Hungary, October 29-30, 2009

27) B. Iván, Cs. Fodor, P. Mezey, G. Kali, A. Domján, R. Thomann, R. Mülhaupt:
Nanohybrids based on Nanophasic Polymer Conetworks: The Application of the Nanoreactor Concept
6th Int Conf. on Nanostructured Polymers and Nanocomposites, Madrid, Spain, April 28-30, 2010

28) Cs. Fodor, G. Kali, K. Z. Perényi, A. Domján, P. Németh, B.Iván:
Poly(*N*-vinylimidazole)-*l*-Poly(tetrahydrofuran) Amphiphilic Conetworks and Their Nanohybrids
3rd EuCheMS European Chemistry Congress, Nürnberg, Germany, August 29 - September 2, 2010 (poster)

29) Fodor Cs., Kali G., Domján A., Németh P., Zihné Perényi K., Bánfi R., Iván B.:
Poli(*N*-vinil-imidazol) alapú amfifil polimer kotérhálók
1st National Konference MKE 2011, Sopron, Hungary, May 22-25, 2011 (poster)

30) Fodor Cs., Iván B.:
Poli(*N*-vinil-imidazol) alapú, nanoszerkezetű amfifil polimer kotérhálók és gélek
HAS Chemical Research Center, Erika Kálmán Scientific Days, Budapest, Hungary, May 26-27, 2011

31) Cs. Fodor, G. Kali, P. Németh, A. Domján, K. Zihné Perényi, B. Iván, R. Thomann, R. Mülhaupt:
Poly(*N*-vinylimidazole)-*l*-Poly(tetrahydrofuran) Amphiphilic Conetworks and Nanohybrids
EuroNanoForum 2011, Budapest, Hungary, May 30 – June 01, 2011 (poszter)